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REMARKS

This Amendment and Response to Non-Final Office Action is being submitted in response to the non-final Office Action mailed March 5, 2004. Claims 5 and 14-17 are pending in the Application. Claims 5 and 14-17 stand rejected under 35 U.S.C. 103(a) as being unpatentable over (obvious from) Friese et al. '007 (U.S. Patent No. 5,181,007) in view of Tani et al. (U.S. Patent No. 5,735,606), Murata et al. (U.S. Patent No. 4,901,051), or Gerblinger et al. (U.S. Patent No. 5,430,428). Claims 5 and 14-17 also stand rejected under 35 U.S.C. 103(a) as being unpatentable over Friese et al. '007 in view of Tani et al., as applied to the claims above, and further in view of Wienand et al. (U.S. Patent No. 5,831,512). Claims 16 and 17 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Friese et al. '007 in view of Gerblinger et al., as applied to the claims above, and further in view of Wienand et al.

In response to these rejections, Claims 5, 16, and 17 have been amended to further clarify the subject matter of the present invention. These amendments are fully supported in the specification, drawings, and claims of the Application and no new matter has been added. Based upon the amendments, reconsideration of the Application is respectfully requested in light of the following remarks.

Rejection of Claims 5 and 14-17 Under 35 U.S.C. 103(a) – Friese et al. '007, Tani et al., Murata et al., and Gerblinger et al.:

Claims 5 and 14-17 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Friese et al. '007 (U.S. Patent No. 5,181,007) in view of Tani et al. (U.S. Patent No. 5,735,606), Murata et al. (U.S. Patent No. 4,901,051), or Gerblinger et al. (U.S. Patent No. 5,430,428).

Specifically, the Examiner states:

Friese discloses the claimed invention at Figs. 1 or 2 except the platinum film resistor 6 being thin film. Tani discloses a platinum film resistor 14 that can be produced by thin or thick film techniques for use as a temperature sensor

(sputtering or screen printing – col. 3, lines 49-52) such that it would have been obvious to employ either type of platinum film where both are known in the temperature sensor resistor arts. Murata at col. 4, lines 1-12 also discloses that the platinum temperature sensing film may be thin or thick for use as a temperature sensor in a multilayered sensor such as that of Friese. One would be motivated to interchange the two depending on the equipment and materials available, or the response desired.¹

As the Examiner correctly notes, Friese et al. do not teach or suggest the use of a platinum thin-film resistor, such as that described and claimed in the present Application. Examiner's assertion that Tani et al. and Murata et al. teach the use of a platinum thin-film resistor and that the use of such a platinum thin-film resistor in conjunction with a multilayered temperature sensor such as that taught by Friese et al. is obvious to one of ordinary skill in the art is clearly incorrect.

As has been argued previously, Friese et al. teach the use of two ceramic films (FILMS 1 and 11, Figs. 1 and 2) that are laminated and sintered in conjunction with two ceramic frames (frames 4 and 4', Figs. 1 and 2). See Friese et al., col. 6, line 36 to col. 8, line 18. Thus, the ceramic films that are laminated and sintered are ceramic green sheets. When laminating and sintering ceramic green sheets, it is not possible to effectively make use of a platinum thin-film resistor.

In the thick film techniques taught by Friese et al., metal or cermet-based suspensions or pastes are applied to produce resistor tracks. See Friese et al., col. 2, lines 32-37. Such a suspension or paste may readily be sintered or fired with a ceramic film (i.e. a ceramic green sheet) onto which the same is applied because the suspension or paste typically has a metal particle content of about 85% or more, the remaining particle content comprising ingredients that volatilize during sintering or firing. Thus, only a small fraction of the suspension or paste volatilizes during sintering or firing.

To produce a thin-film resistor track having a sufficient thickness (of about 1 μm), it is necessary to apply a number of thin layers (each having a thickness of about 0.1 μm) of a thin-film paste, wherein each of the thin layers has to be sintered or fired before the

¹ Non-Final Office Action, p. 2.

next is applied because the thin-film paste typically has a metal particle content of about 15% or less, the remaining particle content comprising ingredients that volatilize during sintering or firing. Thus, a large fraction of the thin-film paste volatilizes during sintering or firing and it is not possible to sinter or fire the thin-film paste with a ceramic film (i.e. a ceramic green sheet).

In response to this argument, the Examiner states:

Applicant argues there is no motivation for a thin film because one would not interchange that with a thick film for various reasons. This argument is contradicted by the prior art of Murata, Tani, and Gerblinger et al., which discloses interchanging thin and thick films in devices very similar to that of Friese – multilayered platinum temperature sensors. One would be motivated to do so depending on the equipment and materials available, or the response desired. If any problem exists with firing the films together, one could have fired the ceramic insulating plates first and then put the thin films on same.²

However, the Examiner overlooks the fact that the use of a platinum thin-film resistor with a multilayered temperature sensor such as that taught by Friese et al. would provide a multilayered temperature sensor that exhibits poor performance characteristics, not fulfilling any meaningful technical standard, and one of ordinary skill in the art would readily dismiss such a combination. Examiner's suggestion that “[i]f any problem exists with firing the films together, one could have fired the ceramic insulating plates first and then put the thin films on same” ignores the fact that Friese et al. teach laminating the ceramic green sheets and, after the lamination process, hermetically sealing the PTC temperature sensor inside a structure. Thus, it would not be possible to sinter or fire the ceramic green sheets and then put the platinum thin-film resistor on the same.

The use of a platinum thin-film resistor in the present invention is possible because two ceramic substrates that have been sintered or fired prior to connecting them by means of a connecting frame made of a glaze comprising a glass are used. Friese et al. teach the application of a thick-film resistor to an insulating layer rather than to the surface of a ceramic substrate. According to Friese et al., the insulating layer may not be omitted in view of the electrical characteristics of YSZ at high temperatures. Also according to Friese

² Non-Final Office Action, p. 4.

et al., the ceramic films 1 and 11 are not connected directly by means of the frames 4 and 4', the insulating layers 3 and 3" being arranged therebetween.

For the above reasons, Applicant submits that the rejection of independent Claim 5 and dependent Claims 14-17 under 35 U.S.C. 103(a) is improper and respectfully requests that the rejection be withdrawn.

Examiner also states:

In Friese, the glaze layer 4 is the connecting layer, described as a frame, such that it is in the border area as a sealing frame. A glaze is “a smooth, thin, shiny coating” Webster’s II, New Riverside University Dictionary. As an alternative, in Gerblinger et al., the glass layer US is used to connect a thin or thick film layer to a ceramic layer, see abstract, for the purpose of protecting the thin film platinum layer, so that it would have been obvious to employ the glaze layer and thin film resistor in the Friese et al. device (thus meeting claim 17 also). The frame of Friese is depicted as a hermetically sealing frame surrounding the resistor 6 in Fig. 2, and described as a frame, see col. 3, lines 53-60, col. 5, lines 21-52. The ceramic cover and ceramic substrate are either 3, or films 1 and 11. The additional layers meet claim 16. See col. 5, line 50-51, col. 4, lines 8-14. In claim 14, the ceramic substrate is alumina. In claim 15, the cover layer 4' at Fig. 2 is alumina. In claim 16, film 11 meets the claim as a cover layer and it is on the peripheral edges, as well as the remaining portions.³

As has been argued previously, the YSZ frames 4 and 4' of Friese et al. do not represent a “glaze” as this term is used in the Application and by those of ordinary skill in the art. A “glaze” is more than “a smooth, thin, shiny coating.” This definition is without reference to any specific context, field, or technique. In the field of sensors and, in particular, temperature sensors, the term “glaze” (as translated from the German term “Glasur”) refers to a glass that has been melted at a specific temperature, and such a “glaze” is characterized by the fact that it may be repeatedly melted at the same temperature. On the contrary, a YSZ green sheet that has been sintered or fired at a specific temperature may not be melted again by heating the YSZ green sheet to the same temperature. Thus, the YSZ frames 4 and 4' of Friese et al. do not represent a “glaze” as this term is used in the Application and by those of ordinary skill in the art.

³ Non-Final Office Action, pp. 2-3.

The above definition of the term “glaze” is supported by the Engineered Materials Handbook, Vol. 4: Ceramics and Glasses, pp. 9,10, and 1061-1068 (1991), prepared by ASM International (copy attached), which states that “[a] glaze is defined as a continuous adherent layer of glass (or glass and crystals) on the surface of a ceramic body that is hard, non-absorbent, and easily cleaned.” The term “glaze” and its use in the Application are now made explicit in amended Claim 5 which recites, in relevant part:

a connecting layer made of a glaze comprising a glass that is applied to the ceramic substrate in a frame-like shape in a border area surrounding the platinum thin-film resistor by means of which the ceramic cover layer is connected with the ceramic substrate in such a way that the platinum thin-film resistor is sealingly encapsulated with regard to the environment, wherein an interior portion of the connecting layer defines a void within which the platinum thin-film resistor is disposed

This defect of Friese et al., in that they do not teach or suggest the use of a connecting layer made of a glaze comprising a glass that is applied to a ceramic substrate in a frame-like shape in a border area surrounding a platinum thin-film resistor by means of which a ceramic cover layer is connected with the ceramic substrate in such a way that the platinum thin-film resistor is sealingly encapsulated with regard to the environment, is not cured by Gerblinger et al., nor by any of the other references cited by Examiner, as Claim 5 has also been amended to recite, in relevant part:

a connecting layer made of a glaze comprising a glass that is applied to the ceramic substrate in a frame-like shape in a border area surrounding the platinum thin-film resistor by means of which the ceramic cover layer is connected with the ceramic substrate in such a way that the platinum thin-film resistor is sealingly encapsulated with regard to the environment, wherein an interior portion of the connecting layer defines a void within which the platinum thin-film resistor is disposed (emphasis added)

Neither Friese et al., Tani et al., Murata et al., nor Gerblinger et al. teach or suggest the use of a frame-like connecting layer made of a glaze comprising a glass, wherein an interior portion of the connecting layer defines a void within which a platinum thin-film resistor is disposed.

According to the present invention, the platinum thin-film resistor is substantially not in contact with any glaze, such that problems with electro-chemical decomposition of protective glazes when in contact with current-carrying thin-film resistors at high temperatures are avoided (see specification, p. 2, lines 6-17; p. 4, line 36 to p. 5, line 19; p. 7, lines 20-26; and p. 8, line 32 to p. 9, line 6). None of the references cited by the Examiner include any hint or suggestion regarding the decomposition problems encountered when making use of a “full area” connecting layer made of a glass. Thus, one of ordinary skill in the art would have no motivation to depart from the usual practice of using such a “full area” connecting layer made of a glass, especially in light of the fact that a “full area” connecting layer made of a glass provides acceptable sealing performance.

For the above reasons, Applicant submits that the rejection of independent Claim 5 and dependent Claims 14-17 under 35 U.S.C. 103(a) has been overcome and is now improper and respectfully requests that the rejection be withdrawn.

Rejection of Claims 5 and 14-17 Under 35 U.S.C. 103(a) – Friese et al. ‘007, Tani et al., and Wienand et al.:

Claims 5 and 14-17 also stand rejected under 35 U.S.C. 103(a) as being unpatentable over Friese et al. ‘007 in view of Tani et al., as applied to the claims above, and further in view of Wienand et al. (U.S. Patent No. 5,831,512).

For the above reasons, Applicant submits that the rejection of independent Claim 5 and dependent Claims 14-17 under 35 U.S.C. 103(a) has been overcome and is now improper and respectfully requests that the rejection be withdrawn.

Rejection of Claims 16 and 17 Under 35 U.S.C. 103(a) – Friese et al. ‘007, Gerblinger et al., and Wienand et al.:

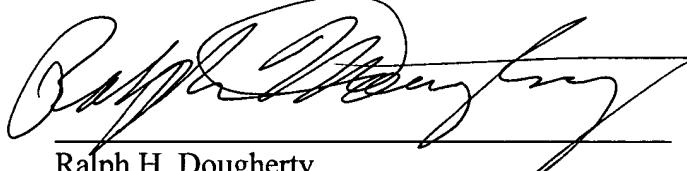
Claims 16 and 17 stand rejected under 35 U.S.C. 103(a) as being unpatentable over Friese et al. '007 in view of Gerblinger et al., as applied to the claims above, and further in view of Wienand et al.

For the above reasons, Applicant submits that the rejection of dependent Claims 16 and 17 under 35 U.S.C. 103(a) has been overcome and is now improper and respectfully requests that the rejection be withdrawn.

Since the amendment to the claims does not add more claims than previously paid for, no additional fee is required.

In view of the foregoing amendment and these remarks, this application is now believed to be in condition for allowance, and such action is respectfully requested on behalf of Applicant.

Respectfully submitted,



Ralph H. Dougherty
Registration No. 25,851
Christopher L. Bernard
Registration No.: 48,234
Attorneys for Applicant
DOUGHERTY, CLEMENTS, HOFER & BERNARD
The Roxborough Building
1901 Roxborough Road, Suite 300
Charlotte, North Carolina 28211
Telephone: (704) 366-6642
Facsimile: 704.366.9744

ENGINEERED MATERIALS HANDBOOK®

Volume 4

CERAMICS AND GLASSES

Prepared under the direction of the
ASM International Handbook Committee

Samuel J. Schneider, Jr., Volume Chairman

Joseph R. Davis, Manager of Handbook Development
Grace M. Davidson, Production Project Manager

Steven R. Lampman, Technical Editor

Mara S. Woods, Technical Editor

Theodore B. Zorc, Technical Editor

Robert C. Uhl, Director of Reference Publications

Editorial Assistance
Heather P. Lampman
Nikki D. Wheaton



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Information Society**

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Overview of Traditional Ceramics / 9

be used as a blank or slug for other forming operations.

Piston extrusion is an intermittent operation in which a prepared batch or a de-aired slug is placed in a cylinder and forced through a die. Pressures up to 50 MPa (7.3 ksi) can be achieved. As is the case with all extrusion operations, only parts that are symmetric to the extrusion axis can be produced.

Auger extrusion is a commonly used continuous operation in which high extrusion pressures are not required. The auger extruder consists of a cylinder, feed screw, and die. The feed screw pushes the batch through the die. It is common to have a pug mill inline with the extruder. A pug mill consists of a trough, fed by a separate de-airing screw that forces the batch through a shredder into a vacuum chamber. The de-aired and shredded batch is then fed by screw into the extrusion cylinder and through the die. Auger extrusion pressures (4 to 15 MPa, or 0.6 to 2.2 ksi) tend to be lower than those used in piston extruders, and a more plastic batch is required.

Pressing is the simultaneous compaction and shaping of a powder or granular mass confined in a rigid die or flexible mold. Pressing can be classified by the direction of pressure application, that is, uniaxial or isostatic.

Uniaxial pressing is what is commonly referred to as die pressing. A die cavity is filled with a measured quantity of powder feed and then is compacted by the action of punches moving along a single axis. Uniaxial pressing can be further classified according to the moisture content of the feed. Dust pressing applies to the compaction of feed containing 5 to 15% moisture at high pressures (140 MPa, or 20.3 ksi), in a steel die. When the moisture content of the feed is reduced to <2%, the compaction is referred to as dry pressing. In dry pressing, higher pressures (200 to 250 MPa, or 29 to 36 ksi) are required than dust pressing. A binder and lubricant are typically employed.

Isostatic pressing involves the application of pressure equally to all surfaces of the feed. An isostatic press consists of a pressure vessel filled with an incompressible fluid. The feed is enclosed in a sealed elastomeric mold, immersed in the fluid, and pressurized. The fluid transfers pressure equally to all sides of the part. Typical pressures are 280 MPa (40.6 ksi).

Slip casting is the process whereby a self-supporting shape is produced by the filtration of liquid from a suspension by the action of porous mold. In this process a slip, or flocculated suspension containing 40 to 55 % solids, is poured into a plaster mold. After a layer has formed, the excess slip is siphoned away. The mold continues to draw water away from the cast layer, allowing the vessel to assume a rigid plastic state, whereupon it may be removed from the mold. This is referred to as drain casting. If the slip is

not drained from the mold and the entire cavity is allowed to solidify, the process is referred to as solid casting.

Structural Clay Products

The use of ceramics in construction dates back more than 4000 years. Urban planners at Mohenjo-Daro in the Indus Valley used fired clay bricks and tile for public buildings, water-supply conduits, and an advanced sewer system. Fired ceramics have been used ever since as structural materials because of their high compressive strength and imperviousness to water penetration. Today, structural clay products constitute over 50% of the entire ceramic industry. Table 8 identifies principal product types and their varied applications. There are many compositions that offer unique

properties specific to their end use. These variations become very large in number if the aesthetics of the product are considered.

The industry is based on improved technologies, rather than improved materials. It can be said that the majority of structural clay products are commodities, rather than specialties. As such, the industry can be considered conservative in that manufacturing issues focus on highly automated processes and on minimizing labor costs.

Materials. With the exception of tile, most structural clay products are coarse-grained ceramics. The primary raw materials are typically located on or near the property of the manufacturing facility. Both clay and argillaceous shale are used with little or no beneficiation, except when the application is tile, for which compositions of beneficiated raw materials are used. Typical bodies contain 35 to 55% clay, 25 to 45% filler, such as silica, and 25 to 55% flux materials. In many cases, the local raw materials contain these constituents in proportions close to that required in the end product. For example, a New Jersey shale deposit contained 67% SiO_2 , 18% Al_2O_3 ; 3% Fe_2O_3 , 2% alkaline earth oxides, and 4% alkalies, with a loss on ignition of 4%. This material, by itself, was found to make a satisfactory brick. The various types and colors of clay minerals used in the United States for structural clay products are:

- Crude, residual, kaolinitic clays; white
- Kaolinitic-illitic fireclays; buff
- Illitic-kaolinitic shales; red
- Illitic clays; red
- Diltic shales; red
- Illitic-chloritic shales; red
- Argillaceous-calcareous clays; pink to buff
- Argillaceous-calcareous shales; pink to buff

The properties of structural clay products vary depending on the type of product, the raw materials used, and the firing conditions. The most important properties tend to be compressive strength and water absorption. For example, paving bricks range in compressive strength from 17 to 137 MPa (2.5 to 20 ksi) and 1 to 6% absorption, while facing brick can have a compressive strength ranging from 4 to 137 MPa (0.6 to 20 ksi) and 2 to 25% absorption. The variation is indicative of the different end uses. Table 9 gives the compressive strength and water absorption for four general types of products.

Glazes

A glaze is defined as a continuous adherent layer of glass (or glass and crystals) on the surface of a ceramic body that is hard, non-absorbent, and easily cleaned. The surface may be shiny or matte. A glaze is usually applied as a suspension of glaze-forming ingredients in water. After the glaze layer dries on the surface of the piece, it is fired, whereupon the ingredients melt to form a thin layer of

Table 8 Classification of structural clay products

I. Bricks
A. Facing
1. Extruded
a. Solid, smooth, textured, or glazed
b. Cored, smooth, textured, or glazed
c. Panel, smooth, textured, or glazed
2. Sand molded, natural, colored, or glazed
3. Dry pressed, solid
B. Paving, solid; extruded
1. Sidewalk, smooth or textured
2. Street or highway, smooth or textured
C. Industrial floor, solid, smooth, or textured; extruded
D. Chimney, extruded
E. Industrial chimney lining; extruded
F. Sewer and manhole; extruded
II. Tiles
A. Structural for walls; extruded
1. Nonload-bearing, smooth or textured
2. Load-bearing, smooth or textured
3. Facing
a. Smooth
b. Textured
c. Glazed
d. Acoustical
e. Lightweight
f. Through-the-wall
4. Screen, smooth or textured
B. Floor
1. Large-cored, smooth or textured; extruded
2. Quarry; plastic pressed
3. Mosaic, unglazed and glazed; dry pressed
C. Wall, unglazed and glazed; dry pressed
D. Roofing; extruded and plastic pressed
E. Flue linings; extruded
III. Pipes, extruded
A. Sewer and drain, plain or glazed
1. Bell and spigot end
2. Plain end
B. Perforated subdrainage
1. Bell and spigot end
2. Plain end
C. Chemical-resistant, plain or glazed
D. Conduit, plain or glazed
E. Drain tile
1. Plain
2. Perforated
IV. Liner plates, curved or flat, plain or glazed
V. Filter blocks for trickling filters, plain, or glazed
VI. Chemical-resistant tower packing
VII. Terra cotta specialty shapes

10/Introduction to Ceramics and Glasses

Table 9 Selected properties of structural clay product types

Product	Compressive strength		Water absorption, %
	MPa	ksi	
Fancy brick	4-137	0.58-20	2-25
Paving brick	17-137	2.50-20	1-6
Structural tile	3.5-69	0.51-10	2-28
	17.5-146	2.53-21	1-8
Drain tile for pipe	10-79	1.43-11	5-16

glass. The glaze may be fired at the same time as the body or in a second firing. Typical glazes can be made to mature from 500 to 1500 °C (930 to 2730 °F), depending on the items to which they are applied.

Glazes are classified as to their optical properties and composition. Glazes tend to be transparent (clear), opaque (enamel), fine interior crystals, or large interior crystals (crystalline). Described below in terms of molar composition are the common types of raw, fritted, and special glazes.

Raw glazes are available in these five compositions: lead-containing, leadless, zinc-containing, porcelain, or slip.

Raw lead glazes are only used on artwork, rather than commercial ware, because of the health hazards associated with soluble lead. A typical bright glaze maturing at cone 05 (1031 °C, or 1890 °F) has the composition of 0.5 PbO, 0.2 Al₂O₃, 1.0 SiO₂, 0.3 CaO, and 0.1 Na₂O.

Leadless glazes are designed to lower the maturity of porcelain glazes without the use of lead oxide (1190 °C, or 2175 °F). A typical glaze has the composition of 0.217 K₂O, 0.352 Al₂O₃, 2.77 SiO₂, 0.454 MgO, 0.454 CaO, 0.135 BaO, and 0.82 SnO₂.

Zinc-containing glazes, sometimes referred to as Bristol glazes, are used on stoneware and terra cotta clayware. They are useful when a lower maturing temperature than is possible with a porcelain glaze is desired, and mature at cone 5 (1175 °C, or 2145 °F). A typical glaze has the composition of 0.36 K₂O, 0.5 Al₂O₃, 3.16 SiO₂, 0.40 CaO, and 0.24 ZnO.

Porcelain glazes are designed to mature in the same temperature range as a porcelain body, cones 8 to 10 (1236 to 1285 °C, or 2255 to 2345 °F). A typical bright glaze has the composition of 0.3 K₂O, 0.58 Al₂O₃, 3.75 SiO₂, and 0.7 CaO. A matte porcelain glaze maturing at the same temperature is made by increasing the alumina and decreasing the silica. Its composition is 0.3 K₂O, 0.65 Al₂O₃, 2.25 SiO₂, and 0.7 CaO.

Slip glazes are natural clays used for artwork glazing and high-tension electrical porcelain insulators. They have a maturing range of 1200 to 1300 °C (2190 to 2370 °F). Their approximate composition is 0.20 K₂O, 0.60 Al₂O₃, 4.00 SiO₂, 0.45 CaO, 0.08 Fe₂O₃, and 0.35 MgO.

Fritted glazes can either contain lead or be leadless. A frit is a glass ground to a fine

powder and used as one of the glaze constituents. The main purpose of fritting is to be able to use water-soluble materials by melting them together to form a relatively insoluble glass. Secondary purposes for fritting are to obtain better working properties of the glaze, to distribute color more uniformly, and to reduce the toxicity of materials such as lead. Fritted glazes, whether lead or leadless, may be totally fritted or partially fritted. The decision to partially frit a glaze, use raw materials with a frit, or to completely frit is usually a cost issue, because frits may increase the cost of the glaze constituents by a factor of ten. Fritted glazes are used for all types of ceramic bodies. A typical leaded frit composition is 0.50 PbO, 0.10 Al₂O₃, 2.70 SiO₂, 0.30 Na₂O, and 0.20 K₂O. A typical leadless fritted glaze containing boric oxide, B₂O₃, which is soluble in water, has the composition of 0.69 CaO, 0.37 Al₂O₃, 2.17 SiO₂, 0.19 Na₂O, 1.16 B₂O₃, and 0.12 K₂O.

Special glazes are available in these four compositions: salt vapor, luster, crystal, or reduction.

Salt glazing is a common method for glazing stoneware and structural clay products. The glaze is formed by throwing common salt, NaCl, into the kiln during the sintering stage of firing. The salt decomposes to form Na₂O and HCl, and the Na₂O combines with Al₂O₃ and SiO₂ on the surface of the product to form a complex silicate glass layer. It is common in firing from cones 5 to 8.

Luster glazes consist of a thin, metallic coating fired on top of a lead-based glaze. The coating is achieved by applying a metallic salt dissolved in an organic resin over a fired glaze. The luster is fired at a low temperature that is high enough to decompose the resin and salt but is lower than the softening point of the glaze. The decomposed resin provides carbon, which acts on the easily reducible oxide to produce the thin, metal film. The metallic salts include bismuth, lead, zinc, cobalt, silver, and gold. The various metal salts produce a variety of reds, yellows, browns, and silvery-white lustres, as well as nacreous and iridescent sheens.

Crystalline glazes are a special type that, under the proper heat treatment, promote crystal growth within the glaze. The most typical glazes are zinc-based, which produce willemite (ZnO-SiO₂) crystals. A formulation that is typical of this type of glaze has 0.235 K₂O, 0.162 Al₂O₃, 1.700 SiO₂, 0.087 CaO, 0.202 TiO₂, 0.032 Na₂O, 0.051 BaO, and 0.575 ZnO.

Applications. Glazes may be applied either wet or dry. The process of wet glaze application entails first preparing the glaze suspension. This is typically done by mixing the glaze constituents in a ball mill. During this operation the ingredients are intimately mixed and the particle size is adjusted. Next, the glaze slurry is screened and passed through magnetic filters, thereby removing any mill residue and ferrous contamination that could

lead to glaze surface defects. Once the glaze suspension is screened, its rheology is adjusted. The glaze is applied to the ware to either painting, pouring, dipping, or spraying, depending on the type of product and the production volume.

Dry glaze application is done in limited instances. In the case of special tile design spray-dried glaze granules are poured over the shape to which an adhesive has been applied such as a carboxymethyl cellulose gum solution. The glaze granules stick to the shape, which is then dried and fired. The advantages of this method are that unique patterns are possible, glaze waste is minimized, and dry time is reduced.

Portland Cement

Cement is a synthetic mineral mixture that, when ground to a powder and mixed with water, forms a stonelike mass. This results from a series of chemical reactions whereby the crystalline constituents hydrate forming a material of high hardness that is extremely resistant to compressive loading. During hydration, cement forms a noncrystalline paste that has good adhesive properties. When the cement paste has set or hardened, it consists of submicron-size crystals in a gel-like material that possess a high surface area value. Cement is characterized by the presence of four main compounds: calcium trisilicate, calcium disilicate, tricalcium aluminate, and tetracalcium aluminoferrite.

The history of cement dates back to the Romans, who found that mixtures of volcanic ash, lime, and clay would harden when wet and used it extensively to build structures. In 1757, it was found that burned and ground calcitic clays would harden when placed in water. In 1824, a patent was granted to a British bricklayer who formulated a new type of cement with improved hardness. Because the color of the material after hydration reminded him of the limestone on the Isle of Portland, he named the product portland cement. This cement was made by lightly calcining small batches of lime and clay and grinding the product to fine powder.

The modern manufacturing process is very basic and has not been radically changed since its inception except for the use of computer-controlled equipment, which has greatly improved the consistency of the final product. In addition, the process has now become more energy efficient and there is less waste of material.

The manufacturing process of cement involves four basic operations: 1) quarrying and crushing of raw materials; 2) grinding high fineness and carefully proportioning the mineral constituents; 3) pyroprocessing of raw materials in a rotary calciner, and cooling and grinding the calcined product, clinker, to obtain a fine powder.

COATING AND SEALING USE

Glazes and Enamels

Richard A. Eppler, Eppler Associates and Laurence D. Gill, Mobay Corporation

VITREOUS CERAMIC COATINGS are applied over substrates for a number of reasons (Ref 1). These coatings may be applied to a substrate surface to render the surface:

- Chemically more inert
- Impervious to liquids and gases
- More readily cleanable
- Smoother and more resistant to abrasion and scratching
- Mechanically stronger
- Decorative
- Aesthetically pleasing

Vitreous coatings are thin layers of glass fused onto the surface of the substrate. When the substrate is a ceramic, the coating is called glaze. When the substrate is a metal, the coating is called a porcelain enamel. When the substrate is a glass, the coating is called glass enamel.

There are two general types of properties that must be present in a ceramic coating (Ref 2). The first requirement derives from the fact that the coating must be applied to and bond with the substrate. The composition must fuse a homogeneous viscous glass at a temperature that is either coincident with the temperature at which the body matures or at a temperature sufficiently lower to prevent distortion of the substrate during glaze firing. During and after fusion of the coating materials, they must react with the substrate to form an intermediate bonding layer of proper thickness. If the bonding layer or interface is too thin, the coating will flake off after application and subsequent firing. If the bonding layer is too thick, the composition of the body or the coating may be degraded. The coating must also have a coefficient of thermal expansion that coincides or fits the substrate (Ref 3). When the fired ware is cooled, the coated substrate contracts. If the coefficients of thermal expansion of the coating and the substrate are not matched, stresses will lead to spalling or crazing of the coating will be introduced. The coating materials should have a low surface tension to minimize the crawling of the coating away from the edges or any holes present during firing. The second group of properties are those associated with the use of the product, such as appearance, smoothness, porosity, and erosion resistance to various liquids and

gases. Almost all vitreous coatings are expected to be homogeneous, smooth, and hard and also to resist abrasion and scratching. Such a surface is also more apt to be impervious to liquids and gases and hence more readily cleanable. The sole exception to the desire for a smooth surface is the textured coating in which a pattern is applied for aesthetic purposes.

In many applications, chemical durability in severe service conditions is a principal reason for the selection of a ceramic coating (Ref 4). Vitreous coatings are formulated to be resistant to a variety of reagents ranging from acids, to hot water, to alkalies, to essentially all organic media. The only important exception is hydrofluoric acid, which readily attacks all silicate glasses.

For some applications, the finished ware is to be subjected to elevated temperatures while in service. This is a prime reason for the selection of ceramic coatings for cookware applications and for industrial and military applications.

The optical and appearance properties of any surface coating material are major considerations in determining which coating will be applied. Various possibilities can be called for to meet the requirements of a particular application. Because vitreous coatings can be transparent or opaque; high gloss, satin, or matte; smooth, patterned, or textured; and monochrome or multicolored, the combination of requirements that meets each particular application is extensive.

Glazes

A ceramic glaze is a vitreous coating applied to a ceramic substrate (usually a whiteware). A great variety of formulations are used as glazes (Ref 1). Ceramic ware is fired over a wide range of temperatures from 800 to $>1400^{\circ}\text{C}$ (1470 to $>2550^{\circ}\text{F}$). No single glaze composition would be satisfactory over such a wide range of temperatures. A glaze that melts at low temperature will run off the substrate, react with the substrate, or volatilize if fired at a high temperature. A given glaze composition is generally useful over a temperature range of only 30°C (55°F). Typical firing temperatures for glazes based on application can be summarized as follows (Ref 5):

- Electronic substrates, ≈ 600 to 900°C (≈ 1110 to 1650°F)
- Artware glazes, ≈ 900 to 1050°C (≈ 1650 to 1920°F)
- Dinnerware and tile glazes, ≈ 1000 to 1150°C (≈ 1830 to 2100°F)
- Structural clay and sanitaryware glazes, ≈ 1180 to 1250°C (≈ 2155 to 2280°F)
- Porcelain glazes, $\geq 1300^{\circ}\text{C}$ ($\geq 2370^{\circ}\text{F}$)

Because of the toxicity of lead, glazes are often classified on the basis of the presence or the absence of litharge (PbO). Safe working practices require unfired glazes containing litharge to be carefully handled and to have an acceptable level of acid resistance in raw powdered form in the work environment. Finished tableware coated with a lead glaze must also possess an acceptable level of resistance to chemical attack.

Another way to classify a glaze is according to the way it is constituted. Raw glazes are prepared from mineral powders (usually oxides or carbonates) and are chemically limited to elements that can be obtained in materials having low water solubility. Frits are prepared to allow the use of water-soluble materials, which are first melted to an insoluble glass, and then quenched and broken up. For a partially fritted glaze, only the soluble materials and sufficient network former to make an insoluble glass are fritted. In an all fritted glaze, all components are melted into the frit except for necessary suspending agents.

Markets for Glazed Ceramics

The total whitewares market in the United States is reported to be \$3,459 billion in 1989 (Ref 6). A breakdown of the U.S. market for products using glazes is shown in the chart of Fig 1.

A ceramic coating typically makes up 10 to 15% of the total manufacturing cost of a ceramic product. The value of the properties provided by the coating usually far outweighs this cost. The protective, functional, and decorative surface that is obtained often serves as a primary selling feature of the end product.

Ceramic glazes find their way into a wide range of applications ranging from coffee mugs to automotive sparkplugs. The major markets for ceramic coatings have different requirements, but one common theme is corrosion resistance and cleanability.

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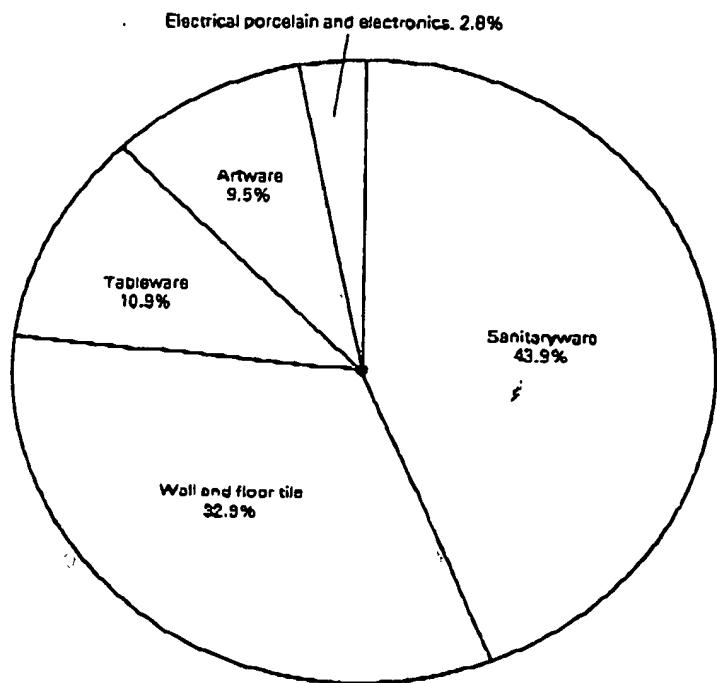


Fig 1 Chart showing breakdown of key segments of the \$3.46 billion glass market in the United States

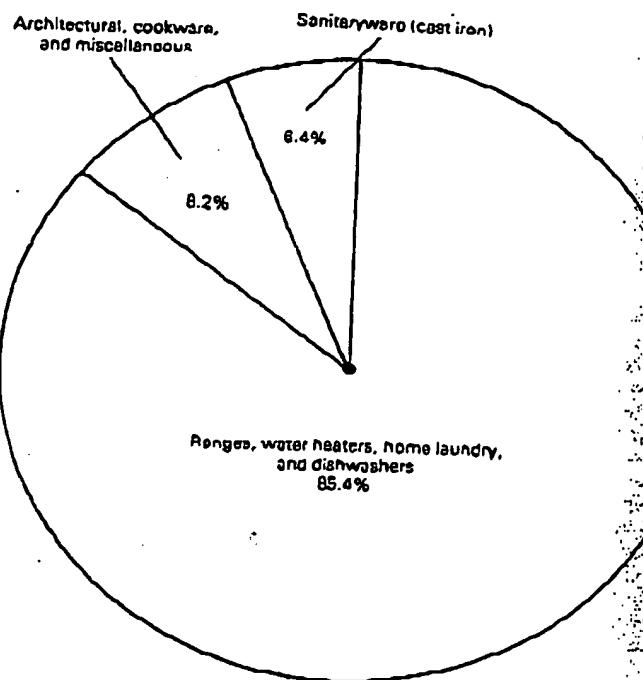


Fig 2 Chart showing breakdown of key segments of the \$5.486 billion porcelain market in the United States

Rarely sold in a ready-to-use form, ceramic glazes are usually formulated and processed for application by the end user.

Role of Specific Oxides in Glazes

The commonly used oxides in glazes are SiO_2 , ZrO_2 , Al_2O_3 , B_2O_3 , CaO , SrO , BaO , MgO , ZnO , PbO , Li_2O , Na_2O , and K_2O (Ref 7). Small amounts of fluorine are sometimes used as a partial substitution for oxygen.

Silicon Dioxide. Most glazes contain more silica than all the other constituents combined. Silica promotes low expansion, high durability, and abrasion resistance. Its only serious deficiency is its high melting point, T_m , of 1723 °C (3133 °F).

Alkali Oxides. The foremost reason for adding other oxides is to reduce the maturing temperature. The alkalis are powerful fluxes at all maturing temperatures, and their use is limited by the high thermal expansion they impart to a glaze.

Alkaline Earths. The alkaline earths and magnesia are effective fluxes only at >1100 °C (>2010 °F).

Zinc oxide is effective at >1000 °C (>1830 °F) and in modest amounts it improves the effectiveness of other fluxes.

Lead monoxide is a powerful flux from the lowest temperatures to >1150 °C (>2100 °F), above which volatilization becomes excessive.

Boric oxide is effective at all temperatures. As a network former, it can be used

with other oxides to get a high fluxing level. Above 15% B_2O_3 concentration, however, it seriously degrades the durability of the glaze.

Alumina contributes to the working properties of a glaze, improves acid durability, and suppresses phase separation and crystallization of the glaze.

Zirconia is added to a glaze to improve the alkaline durability, and, in higher concentrations, as an opacifier.

Leadless Glazes

Tables 1 and 2 give the formulas of a number of commercial ceramic coatings. The first eight of these are leadless glazes. In these glazes, the alkali and alkaline earth oxides, together with MgO , ZnO , and B_2O_3 , are used to provide the fluxing action.

Hard Porcelain Glaze. Glaze 1 is a feldspathic glaze suitable for use only on the highest firing hard paste porcelains (Ref 3).

Soft Porcelain Glaze. For porcelains fired at lower temperatures, such as soft paste porcelain or hard stoneware, glaze 2 would be satisfactory (Ref 8). This glaze is typical of that used on medieval Chinese porcelains.

Sanitaryware Glaze. Glaze 3 is a sanitaryware glaze (Ref 5). It is derived from the soft paste porcelain glaze by the addition of ZnO in large quantities.

Bristol glaze (glaze 4) is used to produce an opaque white coating on stoneware and other dark-colored bodies.

Fast-fire wall tile glazes are derived from the Bristol glaze by increasing the amount of

fluxes to increase the melting rate (Ref 6). Glaze 5 is a typical example.

Semivitreous Dinnerware Glaze. The development of glazes for dinnerware is more difficult because of the lower expansion of the bodies. Glaze 6 is an example of a glaze for semivitreous dinnerware (Ref 10). Several alkaline earths are used to improve melting and surface properties.

Hotel China Glaze. Leadless glazes for vitreous hotel china (such as glaze 7) are very recent development (Ref 11).

Low Expansion Glaze. Zircon and corundum bodies are even lower in expansion requiring a semicrystalline glaze, such as glaze 8 (Ref 12).

Lead-Containing Glazes

Litharge is used in glazes for several reasons (Ref 20). The strong fluxing action of PbO allows the formulation of glazes that mature at temperatures lower than their leadless counterparts, thus leading to greater durability in the formulation of the glaze to obtain low expansion, smooth surface, and maturity of the glaze over a wider firing range. Litharge imparts low surface tension for a smooth surface and a high index of refraction, which results in a brilliant appearance. Glazes containing litharge heal over defects in the glaze surface more readily and are usually more corrosion resistant. This combination of desirable properties is difficult to achieve in leadless glazes on a production scale.

Table 1 Compositions of selected glazes and enamels based on mol-% (Seger formula)

Glazes							
1 Hard porcelain	2 Soft porcelain	3 Sanitaryware	4 Brick	5 Wall tile	6 Semivitreous dinnerware	7 Vitreous dinnerware	
...	0.142	0.100	0.100	0.270	0.081	...	
0.30	0.135	0.100	0.100	0.040	0.115	0.070	
0.043	0.200	0.010	0.066	0.069	
0.70	0.680	0.600	0.400	0.350	0.580	0.037	
...	...	0.200	0.200	0.320	...	0.301	
...	0.110	0.322	
1.00	0.556	0.350	0.400	0.260	0.367	0.039	
10.00	4.570	3.000	3.500	2.650	0.050	0.171	0.188
...	2.721	2.224	
3	8	2	2	9	...	0.011	
					10	11	
Glazes (continued)							
8 Low expansion	9 Cone 4 dinnerware	10 Cone 6C artware	11 Ceramic	12 Opacified	13 Zinc matte	14 Lime matte	
0.800	...	0.179	0.157	...	0.087	0.040	
0.150	0.066	0.083	0.032	0.059	
...	0.494	0.218	0.097	...	
...	0.407	0.152	0.524	
...	0.371	0.364	...	
...	0.261	0.625	1.000	0.028	
0.740	0.340	0.273	...	0.406	0.463	0.377	
0.200	0.314	0.507	...	0.143	0.142	0.262	
2.510	3.369	2.792	0.500	2.019	1.566	0.176	
...	...	0.023	...	0.248	0.210	1.746	
32	13	14	15	16	3	0.211	
					2		
Enamels							
15 Ground eng.	16 Home laundry	17 Bat-water tank	18 Continuous clean coating	19 Opaque cover coat	20 Semimopaque cover coat	21 Clear cover coat	22 Architectural cover coat
0.065	0.085	0.135	0.031	0.127	0.129	0.198	...
0.470	0.638	0.079	0.347	0.646	0.486	0.665	0.220
0.054	0.052	...	0.046	0.277	0.341	0.137	0.680
...	0.014
0.244	0.157	0.110	0.034
...	0.010	0.047	0.007	...
0.105	0.015	0.011	...	0.045	...	0.103	...
0.014	0.015	0.019	0.001
0.038	0.013	...	0.001
0.008	0.518
0.138	0.354	0.060	1.105	0.094	0.046	0.090	0.044
0.489	0.721	0.330	0.050	0.986	0.833	0.344	0.402
...	0.024
...	0.003	0.008
1.623	2.171	2.820	1.186	2.902	2.730	3.313	2.026
...	0.162	0.280	0.173	0.215	0.070
...	0.100	...	0.001	1.117	0.582	0.151	0.807
0.005	0.024	0.003	0.001
0.011	0.010	0.039	0.011
...	0.001
...	0.001
0.316	0.381	0.349	0.112	0.910	0.724	0.417	0.082
2	17	17	18	19	19	2	2

ever, litharge also has disadvantages as constituent. Lead glazed ware must be in a strongly oxidizing atmosphere as lead is readily reduced. Lead oxide can be used above 1150 °C (2100 °F) due to stability. Most importantly, litharge is toxic. Moreover, lead poisoning is very

difficult to diagnose because its symptoms are similar to other ailments. Therefore, every possible precaution must be taken when preparing lead glazes to avoid poisoning, and ware intended for food contact should be tested as noted below to ensure consumer protection.

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Cone 4 Dinnerware Glaze. Glaze 9 in Tables 1 and 2 is an example of a lead-containing dinnerware glaze for cone 4 (1100 °C, or 2010 °F) (Ref 13).

Cone 06 Artware Glaze. Glaze 10 is an example of a clear glaze suitable for use on artware and hobbyware bodies at cone 06 (1000 °C, or 1830 °F) (Ref 14).

Electronic Glaze. The glazes used on alumina packages for integrated circuits (ICs) to seal the package represent the lowest firing lead-containing glazes. Glaze 11 is an example of such a glaze, which can be fired as low as 550 °C (1020 °F) (Ref 15).

Heavy-Metal Release

If lead-containing glazes are not properly formulated, they may be less resistant to acid attack, which results in the release of lead. If such glazes are used in contact with food or drink, lead poisoning of the user may result. Cadmium oxide, which is considerably more toxic than lead oxide (Ref 21), is only used in ceramic coatings in connection with the use of cadmium sulfoselenide pigments, which already contain large amounts of cadmium.

To control this problem under production conditions, standard tests have been developed for determining the lead and cadmium content released from glazed surfaces (Table 3). A sample is exposed to a 4% acetic acid solution for 24 h at room temperature while covered. The concentration in ppm of lead and cadmium in the solution is then determined.

FDA Guidelines. The current United States Food and Drug Administration (FDA) standard limits for lead released are 7 ppm average for six samples of flatware, 5 ppm maximum of six samples of small holloware, and 2.5 ppm maximum of six samples of large holloware (Ref 24). The standard limits for Cd are 1/2 ppm average for six samples of flatware, 1/4 ppm maximum of six samples of small holloware, and 1/4 ppm maximum of six samples of large holloware. These limits are currently under review, and lower levels may possibly be applicable by the time this article is published (Ref 25). Because of statistical fluctuations in the measurements, operating standards must be less than half these guideline values (Ref 26).

In the FDA test, lead-containing commercial dinnerware glazes usually release 1/2 to 2 ppm (Ref 20). Properly designed commercial artware will be somewhat higher. In contrast, ware implicated in health cases have all released in excess of 50 ppm Pb.

Most glazes have no added cadmium oxide. Those that do contain cadmium will release 0.1 to 0.2 ppm even when properly formulated (Ref 21). For this reason, it is best if CdS-Se colors are not used as surface decorations on glass surfaces that will come in contact with food or drink.

The issue of lead and cadmium release from glassware decorated with glass enamels has

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Table 2 Compositions of selected glazes and enamels based on weight percent

Oxide	Glazes						
	1 Hard porcelain	2 Soft porcelain	3 Sanitaryware	4 Ceramic	5 Ware ware	6 Semivitreous dinnerware	7 Vitreous dinnerware
Li ₂ O	...	2.24	2.05	1.98	...	0.51	...
Na ₂ O	...	3.24	3.12	3.01	6.54	1.81	1.81
K ₂ O	3.67	3.24	3.12	3.57	4.47	3.92	2.71
MgO	...	0.44	...	2.57	0.16	0.96	0.62
CaO	5.10	9.71	11.15	7.16	7.67	11.76	9.16
ZnO	5.39	5.19	10.18	...	10.94
SrO	4.12	3.07
BaO	2.50
Al ₂ O ₃	15.24	14.44	18.58	13.01	10.36	13.53	7.37
B ₂ O ₃	1.36	4.30	5.47
SiO ₂	78.00	69.90	59.71	67.09 ^b	62.25	59.09	55.79
ZrO ₂	0.57

Glazes (continued)

Oxide	8 Low expansion	9 Cone 4 dinnerware	10 Cone 06 artwork	11 Electronics	12 Opacifiers	13 Zinc matte	14 Lime matte
Li ₂ O	9.08
Na ₂ O	...	3.00	2.46	...	2.50	1.91	0.83
K ₂ O	5.03	1.72	3.84	1.73	1.91
MgO	1.38	...
CaO	...	7.65	3.09	...	8.29	9.02	10.08
ZnO	10.97	10.48	...
BaO	1.56
PbO	...	16.08	35.30	88.14	...	19.52	28.87
Al ₂ O ₃	26.98	9.57	7.04	...	15.04	15.99	9.17
B ₂ O ₃	4.98	6.04	8.93	...	3.62	3.50	4.20
SiO ₂	53.91	55.88	42.45	11.60	44.07	33.31	35.00
ZrO ₂	0.72	...	11.10	9.16	8.92

Enamels

Oxide	15 Ground glass	16 House laundry	17 Hot-water tank	18 Continuous clean coating	19 Opaque cover coat	20 Semisilicate cover coat	21 Clear cover coat	22 Architectural cover coat
Li ₂ O	0.88	0.81	1.33	0.52	0.59	1.10	1.76	...
Na ₂ O	13.15	12.60	13.92	7.30	9.41	8.58	12.23	4.31
K ₂ O	2.30	1.56	...	1.47	6.13	9.15	3.83	19.70
MgO	...	0.18
CaO	6.18	2.80	2.04	0.65
ZnO	...	0.26	1.27	0.12
BaO	7.27	0.79	0.56	1.04	...	4.15
CoO	0.47	0.36	0.47	0.03
NiO	0.29	0.31	0.03
CuO	0.20	0.03	13.99
Al ₂ O ₃	6.25	11.50	2.02	41.38	2.25	1.34	2.72	1.39
B ₂ O ₃	15.37	15.99	7.60	1.18	16.13	16.53	7.11	8.65
Cr ₂ O ₃	1.24
Sn ₂ O ₃	0.30	0.72
SiO ₂	44.01	41.55	56.05	24.20	40.97	46.74	59.07	37.61
ZrO ₂	...	6.36	11.66	7.24	7.86	2.67
TiO ₂	...	2.55	...	0.03	20.97	13.25	3.58	19.93
MnO ₂	0.20	0.66	1.01	0.03
P ₂ O ₅	0.70	0.45	1.30	0.48
Nb ₂ O ₅	0.06
WO ₃	0.05
MoO ₃
F	2.71	2.31	3.10	0.72	3.17	3.92	2.35	0.48

also been addressed through a voluntary quality-control program adopted by the ceramic industry (Ref 27). The lip and rim area (that is, the top 20 mm, or $\frac{2}{3}$ in.) of the decorated glass must not leach greater than 50 ppm Pb or 3.5 ppm Cd when analyzed by a mod-

ification of the existing ceramic ware test (see Table 3). Failure of one glass in a sample of six is cause for rejection.

Numerous factors must be considered in formulating and processing a glaze to achieve low lead and cadmium release:

- Total glaze composition
- Thermal history during processing
- Glaze application techniques
- Glaze-body solution at the interface during firing
- Atmospheric conditions that exist during firing

Of all these parameters, the most important is the glaze composition.

Heavy-Metal Release Performance Rating. A figure of merit (FM) has been developed to predict the heavy-metal release or acid resistance of a glaze from its composition (Ref 14). Silica, alumina, zirconia, and similar ions such as titania and tin dioxide are effective in lowering the lead release of a glaze:

$$\text{Good} = 2[\text{Al}_2\text{O}_3] + [\text{SiO}_2] + [\text{TiO}_2] + 2[\text{ZrO}_2] + [\text{SnO}_2]$$

The concentrations given in Eq 1 are expressed in molar ratio. The factor 2 arises from the fact that there are 2 equivalents of aluminum ions per equivalent of Al₂O₃.

It has also been shown that alkali line earths, B₂O₃, fluoride, phosphate, CdO, and PbO are all more or less detrimental to the lead release in a glaze:

$$\begin{aligned} \text{Bad} = & 2([\text{Li}_2\text{O}] + [\text{Na}_2\text{O}] + [\text{K}_2\text{O}] \\ & + [\text{B}_2\text{O}_3] + [\text{P}_2\text{O}_5]) + [\text{MgO}] + [\text{CaO}] \\ & + [\text{SrO}] + [\text{BaO}] + [\text{F}] + [\text{ZnO}] \\ & + [\text{PbO}] \end{aligned}$$

Combining these terms gives the figure of merit:

$$\text{FM} = \text{Good}/(\text{Bad})^{1/2}$$

When the figure of merit is > 2.05 , lead release is below the standard. When < 1.80 , some measurements are always higher than the standard. This figure of merit applies to all single-phase glazes. In a glass-ceramic system, the formulation of the refractory basic component must be used in the calculation.

Table 3 Standard test method for determining the lead and cadmium content released from glazed ceramic enamel surfaces used for food preparation when exposed to attack by acetic acid

ASTM standard	Test method
C 738	Lead and cadmium extracted from glazed ceramic surfaces
C 872	Lead and cadmium release from porcelain enamel surfaces
C 895	Lead and cadmium extracted from glazed ceramic dic
C 927	Lead and cadmium extracted from the lip and rim area of glazed ceramic surfaces externally decorated with ceramic glass enamels
C 1034	Lead and cadmium extracted from glazed ceramic cookware

Opaque Glazes

In opaque glazes, the transmittance of the glaze has been reduced to hide the body. Opacity is introduced into ceramic coatings by the addition of a substance that will disperse in the coating as discrete particles to scatter and reflect the incident light (Ref 5). This dispersed substance must have a refractive index that differs from that of the clear ceramic coating.

The refractive index, n_D , of most glasses is 1.5 to 1.6. Typical opacifiers include SnO_2 ($n_D = 2.04$), ZrO_2 ($n_D = 2.40$), ZrSiO_4 ($n_D = 1.85$), and TiO_2 ($n_D = 2.5$ for anatase and 2.7 for rutile). Opacified glaze (glaze 12) in Tables 1 and 2 is an example of a glaze fired at $>1000^\circ\text{C}$ ($>1830^\circ\text{F}$) where zircon is the opacifier of choice (Ref 16).

In coatings fired at $<1000^\circ\text{C}$ ($<1830^\circ\text{F}$), anatase in the anatase phase is the best opacifier because of its high refractive index. The temperature limit is the point at which anatase inverts to rutile. Rutile crystals are unsuitable because they grow too large in glass for opacification and then have a yellow color.

Satin and Matte Glazes

Satin and matte effects are also due to dispersed crystals in the glaze (Ref 5). The crystals must be very small and evenly dispersed if the glaze is to have a smooth velvet appearance. Matte glazes are always somewhat opaque. The amount of opacity depends on the difference in refractive index between glaze and crystal and can be fairly small. Glaze 13 in Tables 1 and 2 is an example of a zinc satin glaze where the crystal is willemite (Zn_2SiO_4) (Ref 2). Glaze 14 is a lime matte glaze with a wollastonite (CaSiO_3) crystal.

Porcelain Enamels

The total market for porcelain enameled products in the United States was reported to be \$4.86 billion in 1989 (Ref 28). The U.S. market breakdown is shown in Fig 2.

Similar to ceramic glazes, porcelain enamels provide an easy-to-clean corrosion-resistant surface for many consumer products. While the coating is primarily functional, the use of color provides an added sales feature, particularly in the architectural market. Overall corrosion resistance is important; alkali resistance and resistance to hot water corrosion are primary concerns for laundry, sanitaryware, and hot-water applications, while acid resistance comes to the forefront in coatings intended for ranges, architectural panels, and cookware.

Porcelain enamel coatings are rarely sold ready-to-use. Conventional porcelain enamel coatings are prepared in an aqueous system by ball milling and applied to the substrate by spray, dip, or flow coating. The coating is allowed to dry before firing. Newer technology involves dry application of powdered porcelain enamel by electrostatic spraying. This dry application eliminates the waste dis-

posal problems associated with wet ball milling, subsequent application, and the washing and cleaning steps.

Adherence

A porcelain enamel must not only act as a protective and aesthetically pleasing surface, but it must also bond to the metal substrate. For proper adherence of the enamel to the metal, it is necessary to develop a continuous electronic structure or chemical bond across the interface (Ref 29). This continuity requires that both the enamel coating and the substrate metal be saturated at the interface with an oxide of the metal (Ref 30). This oxide, which for iron and steel substrates is ferrous oxide (FeO), must not be reduced by the metal when it is in solution in the glass.

Surface roughness also generally improves adherence by creating a greater contact area, but it is of little value if the chemical bond is weak.

To develop a continuity of atomic and electronic structure between an enamel and a metal substrate, a compatible transition layer is needed that is in equilibrium with both the metal substrate and the glass coating at the interface (Ref 29). This zone must include at least a monomolecular layer of an oxide of the metal and is stable only when both the metal and the glass at the interface are saturated with this metal oxide.

Certain transition metal oxides (for example, CoO , NiO , and CuO) can be added to an enamel formulation to improve the adherence between the metal and the substrate. These oxides increase the rate of the reactions in the adherence process and stabilize the saturation of the interface with the critical oxide. Ground coat enamels contain adherence oxides while cover coat enamels lack adherence oxides.

Ground Coat Enamels

Enamel 15 in Tables 1 and 2 is a typical example of a general-purpose ground coat enamel. These enamels are alkali borosilicates that contain small amounts of the adherence oxides to promote the bonding process. In addition to adherence, these coatings provide a chemically protective layer that minimizes surface defects.

Ground coat frits can also be formulated for particular end-use purposes.

Home Laundry Enamel. Enamel 16 in Tables 1 and 2 is a home laundry enamel that has been formulated for outstanding alkali resistance through the addition of large quantities of ZrO_2 (Ref 17).

Hot-Water Tank Enamel. An application with very stringent thermal and corrosion resistance requirements is a hot-water tank. Enamel 17 in Tables 1 and 2 is a hot-water tank enamel. The higher concentration of SiO_2 and the lower concentration of B_2O_3 , reflect the higher firing temperature necessary to obtain the requisite thermal and chemical resistance properties.

Continuous Clean Coating. Enamel 18 in Tables 1 and 2 is a continuous clean coating that has been developed to provide a means of volatilizing and removing food soils from the internal surfaces of ovens during normal operation (Ref 18).

Cover Coat Enamels

Cover coat porcelain enamels are formulated to provide specific color and appearance characteristics, abrasion resistance, surface hardness, resistance to corrosion, and heat and thermal shock resistance. These enamels can be clear, semiopaque, or opaque depending on the application:

- Opaque enamels for white and pastel coatings
- Semisolid enamels for most medium-strength colors
- Clear enamels to produce strong bright colors

Opaque cover coat enamels (for example, enamel 19 in Tables 1 and 2) are opacified with TiO_2 (Ref 19, 31, 32). Usually, all the TiO_2 is melted into a clear frit. During the firing process, this frit partially crystallizes to provide the required opacification. The enamels have excellent acid resistance and fairly good alkali resistance with reflectances ranging from 78 to 88%.

Semisolid Cover Coat Enamel. Enamel 20 in Tables 1 and 2 is an example of a semisolid cover coat enamel. These materials do not differ qualitatively from fully opaque enamels. The concentration of TiO_2 is reduced to the level at which the system is compatible with the use of pigments.

Clear cover coat porcelain enamels such as Enamel 21 in Tables 1 and 2 are used in conjunction with appropriate pigments for the production of strong and medium-strength colors and are similar to ground coat formulations without the adherence oxides.

Architectural Cover Coat Enamels. The architectural siding industry requires cover coat enamels of low gloss and good weatherability/durability. Enamel 22 in Tables 1 and 2 is an example of an enamel for this application. The high zinc oxide concentration is the source of the low gloss finish imparted to the coating.

Glass Enamels

Glass enamels are applied to glass for decorative purposes and not to improve chemical durability or cleanability. Because these coatings are matured at temperatures below the deformation point of the glass substrate (540 to 650°C , or 1000 to 1200°F) and require larger quantities of fluxing elements, corrosion resistance can be difficult to obtain.

Glass enamels are produced in ready-to-use form (for example, paste, thermoplastics, spray media, and ultraviolet curable media) by a few select manufacturers. These enamels are rarely compounded by the end user and represent a specialty product that is more

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akin to organic paints than to other ceramic coatings.

The markets for this specialty product are categorized as tableware, glass containers, architectural, lighting, and automotive. There are no published figures on the value of the specific portion of the glass market that is decorated with glass enamels.

As supplied to the user, glass enamels are mechanical mixtures of pigments (see the section "Ceramic Decoration" in this article), fluxes, and organic suspending media. The requirement for low maturing temperatures necessitates the use of very high lead-oxide containing borosilicates for the flux. The industry relies on in-house control tests to ensure acceptable levels of lead release from decorated areas that might come in contact with food or drink (see the section on "Heavy-Metal Release" in this article).

The organic suspending media for glass enamels are similar to materials used to make organic paints.

Ceramic Decoration

Techniques for Coloring Vitreous Coatings. There are a number of ways to obtain color in a ceramic coating (Ref 33). In one method, certain transition metal ions can be melted into a glass when it is made. While suitable for bulk glass, this method is rarely used for coatings because adequate tinting strength and the purity of color cannot be obtained by this process.

A second method to obtain color is to induce the precipitation of a colored crystal in a transparent matrix. Certain materials dissolve to some extent in a vitreous material at high temperature. When the temperature is reduced, the solubility is also reduced and precipitation occurs. This method is used for opacification (that is, the production of an opaque white color). Normally, some or all of the opacifier added to the coating dissolves during the firing process and recrystallizes upon cooling. For oxide colors other than white, however, this method lacks the necessary control for reproducible results and is seldom used.

The third method to obtain color in a vitreous matrix is to disperse in that matrix one or more insoluble crystals that are colored. The color of the crystal is then imparted to the transparent matrix. This method is the one most commonly used to introduce color to vitreous coatings.

Pigment Systems. To be suitable as a ceramic pigment, a material must have a high tinting strength, a high refractive index, and be free of grayness. It must also possess stability under the high temperatures and corrosive environments encountered in the firing of glazes (Ref 32). Most ceramic pigments are complex oxides (see Table 4) with the lone exception being the cadmium sulfoselenide red pigments.

Table 4 Inorganic pigments to impart colors to ceramic coatings (Ref 33, 34)

Pigment system	CAS registry number(s)	Chemical formula(s)	DCMA no.
Pink and purple			
Chrome-alumina-pink spinel	68201-65-0	Zn(Al,Cr) ₂ O ₄	12
Chrome-alumina-pink corundum	68187-27-9	(Al,Cr) ₂ O ₃	12
Manganese-alumina-pink corundum	68186-99-2	(Al,Mn) ₂ O ₃	12
Zirconium-iron pink zircon	68187-13-3	(Zr,Fe)SiO ₄	12
Chrome-tin orchid cassiterite	68187-53-1	(Sn,Cr) ₂ O ₃	12
Chrome-tin pink spinel	68187-12-2	Cr ₂ O ₃ Sn ₂ O ₃ :Cr	12
Brown			
Zinc-iron-chromite brown spinel	68186-88-9	(Zn,Fe)(Fe,Cr) ₂ O ₄	12
Iron-chromite brown spinel	68187-09-7	Fe ₂ Cr ₂ O ₄	12
Iron-lithium brown spinel	68187-02-0	Fe ₂ TiO ₄	12
Nickel-ferrite brown spinel	68187-10-0	NiFe ₂ O ₄	12
Zinc-ferrite brown spinel	68187-51-9	(Zn,Fe)Fe ₂ O ₄	12
Iron brown hematite	68187-33-9	Fe ₂ O ₃	12
Chrome-iron-manganese brown spinel	68323-00-6	(Fe,Mn)(Fe,Cr,Mn) ₂ O ₄	12
Chromium-manganese-zinc brown spinel	71750-83-9	(Zn,Mn)Cr ₂ O ₄	12
Yellow			
Zirconium-vanadium yellow baddeleyite	68187-01-9	(Zr,V) ₂ O ₅	12
Tin-vanadium yellow cassiterite	68186-93-6	(Sn,V) ₂ O ₅	12
Zirconium-praseodymium yellow zircon	68187-15-5	(Zr,Dy)SiO ₄	12
Lead-antimonate yellow pyrochlore	68187-20-2	Pb ₂ Sb ₂ O ₇	12
Nickel-antimony-titanium yellow rutile	71077-18-4	(Ti,Ni,Sb) ₂ O ₇	12
Nickel-niobium-titanium yellow rutile	68611-43-8	(Ti,Ni,Nb) ₂ O ₇	12
Chrome-antimony-titanium buff rutile	68186-90-3	(Ti,Cr,Sb) ₂ O ₇	12
Chrome-niobium-titanium buff rutile	68611-42-7	(Ti,Cr,Nb) ₂ O ₇	12
Chrome-tungsten-titanium buff rutile	68186-92-5	(Ti,Cr,W) ₂ O ₇	12
Manganese-antimony-titanium buff rutile	68412-38-4	(Ti,Mn,Sb) ₂ O ₇	12
Green			
Chromia-green hematite	68909-79-5	(Cr,Fe) ₂ O ₃	12
Cobalt-chromite blue-green spinel	68187-11-1	Co(Al,Cr) ₂ O ₄	12
Cobalt-chromite green spinel	68187-49-5	Co ₂ O ₃	12
Cobalt-titanate green spinel	68186-85-6	Co ₂ TiO ₄	12
Vitrovia green garnet	68553-01-5	3CaO ₂ Cr ₂ O ₃ :3SiO ₂	12
Nickel-silicate green olivine	68515-84-4	Ni ₂ SiO ₄	12
Blue			
Cobalt-aluminate blue spinel	68186-86-7	CoAl ₂ O ₄	12
Cobalt-zinc-aluminate blue spinel	68186-87-8	(Co,Zn)Al ₂ O ₄	12
Cobalt-silicate blue olivine	68187-40-6	Co ₂ SiO ₄	12
Cobalt-zinc-silicate blue phenacite	68412-74-8	(Co,Zn) ₂ SiO ₄	12
Cobalt-tin blue-gray spinel	68187-05-3	Co ₂ SnO ₄	12
Cobalt-tin-alumina blue spinel	68608-09-3	CoAl ₂ O ₄ /Co ₂ SnO ₄	12
Zirconium-vanadium blue zircon	68186-93-8	(Zr,V)SiO ₄	12
Black			
Iron-cobalt black spinel	68187-50-8	(Fe,Co)Fe ₂ O ₄	12
Iron-cobalt-chromite black spinel	68186-97-0	(Co,Fe)(Fe,Cr) ₂ O ₄	12
Manganese-ferrite black spinel	68186-94-7	(Fe,Mn)(Fe,Mn) ₂ O ₄	12
Copper-chromite black spinel	68186-91-4	CuCr ₂ O ₄	12
Chromium black hematite	68909-79-5	(Cr,Fe) ₂ O ₃	12
Chromium-iron-nickel black spinel	71631-15-7	(Ni,Fe)(Cr,Fe) ₂ O ₄	12
Gray			
Cobalt-nickel gray periclase	68186-89-0	(Co,Ni)O	12
Titanium-vanadium-antimony gray rutile	68187-00-8	(Ti,V,3b) ₂ O ₇	12
Tin-antimony gray cassiterite	68187-54-2	(3n,3b) ₂ O ₇	12

(a) CAS, Chemical Abstract Service. (b) DCMA, Dry Color Manufacturers' Association.

Red Pigments. Orange, red, and dark red colors are obtained only by the use of the cadmium sulfoselenide pigments (Ref 21, 35). Because cadmium compounds are highly toxic (Ref 36), the cadmium sulfoselenide pigments should not be used in applications that will come in contact with food and drink. Moreover, these pigments must also be han-

dled with great care to avoid the possibility of ingestion.

Pink and Purple Pigments. Chromia-alumina pinks (Ref 37) impart pink shades to glazes suitably formulated. The manganese-alumina pink is a very pure clean pink, but it is difficult to manufacture. The most popular pink pigment is the iron-doped zircon.

(Ref 38) in which the shades of color extend from pink to coral. The chrome-tin system is the only family that can produce purple and green shades as well as a pink shade (Ref 39).

Brown Pigments. The zinc-iron-chromite enamel (Ref 40) produce a wide palette of tan and brown shades. The other browns are variations of this system for specific applications.

Yellow Pigments. Zirconia vanadia yellows are economical pigments for use with coatings fired at $>1000^{\circ}\text{C}$ ($>1830^{\circ}\text{F}$) when tinting strength is not required (Ref 41). Vanadium yellows are a strong yellow color but are very costly to produce (Ref 42). Praseodymium zircon pigments have excellent tinting strength in coatings fired to as high as cone 10 (Ref 38). For lower-temperature applications, the tinting strength of lead antimonate pigment is unsurpassed with the exception of the cadmium sulfoselenides. The rutile pigments yield yellow, orange yellow, or maple shades useful in porcelain enamels and glass enamels.

Green Pigments. Green Cr_2O_3 may be used in few applications (Ref 43). The zinc-alumina-chromite bluegreen pigments give shades from blue to blue-green when used in strong tones. The Victoria green gives a translucent bright green color. Because of difficulties inherent in the use of chromium-containing pigments, many green ceramic glazes are now made with zirconia pigments (Ref 38). Stable greens are obtained with a ratio of about 2 parts of the praseodymium zircon yellow to 1 part of the vanadium zircon blue.

Blue Pigments. Cobalt blues, both the spinel (CoAl_2O_4) and the silicate (Co_2SiO_4) forms, are highest tinting strength colors used in glazes (Ref 44). At the higher firing temperatures used for ceramic glazes, they often exhibit a bleeding defect. At these specific temperatures, the vanadium-doped zircon blue is used (Ref 38).

Black Pigments. Black ceramic pigments are formed by mixtures of several oxides to form the spinel structure (Ref 45). The one exception is the chromium black hematite, an expensive pigment suitable for use in zinc-coatings (Ref 46).

Gray Pigments. The cobalt-nickel gray glaze uses zirconia or zircon as a carrier for various ingredients of blacks such as cobalt, iron, and chromium oxides. The titanium-rutile can be used in porcelain enamels.

Ceramic Application In Coatings. When selecting pigments for a specific coating application, consideration must be given to the following parameters (Ref 47):

Processing stability requirements
Coat uniformity and reproducibility
Particle size distribution
Compatibility of all materials to be used
Engobe or body stain must be stable to

the bisque fire. An underglaze color or a colored glaze must be stable to the glost fire and to corrosion by the molten glaze ingredients. An overglaze or glass enamel must only be stable to the decorating fire and to corrosion by the molten flux used in the application.

For most ceramic pigments, uniform and reproducible manufacture requires great care. To avoid specking in a blend, no component should be $<10\%$ of the mix.

Most calcined ceramic pigments are in the 1 to 10 μm (40 to 400 μm) range in mean particle size, with no residue on a 325 mesh (44 μm) screen. The optimum particle size for an application is the largest size that gives uniform dispersion and adequate strength in opacified coatings.

A ceramic pigment must function as a component in a glaze or porcelain enamel system. Thus, it must be compatible with the other components (that is, the glaze itself, the opacifier(s), and the other additives).

Cost Factors and Product Availability

Owing to the limited market and the variety and complexity of the products, ceramic pigments are manufactured by specialty firms and not by the users. The principal producers are Ceramic Color and Chemical Corporation, Drakenfeld Colors Division of Ciba-Geigy Corporation, Englehardt Corporation, Ferro Corporation, General Color and Chemical Corporation, O. Hommel Company, Mason Color and Chemical Corporation, and Mobay Corporation. The cost of ceramic pigments ranges from \$9 to \$50/kg (\$4 to \$20/lb) or even higher, depending on the elemental composition and the processing required.

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